**Fine Structure Corrections**

**Fine structure corrections of the Hydrogenic atom**

Now we’ve covered the basics of the Hydrogen atom, but there is actually more to the interaction between the nucleus and the electron than is apparent. We missed them because we are using the non-relativistic Schrodinger equation. None the less, we can study these relativistic effects using our non-relativistic Schrodinger equation, as long as the additional interactions are small. Hopefully, at the end of the course, we’ll get to the Dirac equation (the relativistic generalization of the Schrodinger equation) which will naturally incorporate these effects into a seamless relativistic framework.

**Correction due to relativistic kinetic energy**

The first relativistic correction we’ll take up has to do with the difference between a particle’s actual kinetic energy and the classical approximation we’ve been using. So a particle’s kinetic energy is:



Taylor expanding this for small v’s we get:



The first term is obviously our classical approximation to the kinetic energy, and the second term is the first order relativistic correction. To incorporate this term into our quantum mechanical description of an electron in a Hydrogenic atom we need to write this KE out in terms of momentum. But we cannot simply say that p = mv because that is only the classical version of p. The relativistic p is…



Now we need to write the KE in terms of the momentum in order to facilitate the QM description of the electron. The way to do this is to solve for the momentum in terms of the velocity, and then plug it into the KE equation. But how do we solve for v in terms of p when the RHS of the equation is an infinite power series in v? A useful technique for this is called series reversion. We assume that we can write v as a power series in p and then plug this expansion into the equation relating v and p, and solve for the coefficients. So write,



Plug this into…



Now this equation must be true for all powers of p and so equating the coefficients of each power of p we get:



so this tells us that:



This is our desired expansion of v in terms of p. And so filling this into the expression for the kinetic energy we get:



So there we go. And the perturbation on our Hamiltonian is:



Of course we could’ve done this more directly by Taylor expanding the following equation,



but sometimes the series reversion stuff is the only route to take and it’s a good technique to know. Alright, now the QM description of the electron would be:



We would like to determine the energy levels of this new Hamiltonian. One possibility would be to write down our energy level equation in the position/spin basis and try to solve for the wavefunctions and energy levels. We would have:



We do have spherical symmetry, again, and perhaps we could go to spherical coordinates and try separation of variables, etc. to get the energy levels. But that would be a lot of work for very little return, because the energy levels of the new Hamiltonian ought to be very close to the old ones (since the relativistic corrections are called the *fine* structure corrections). In this case, a better approach would be to use some approximate technique. We could use the RS perturbative technique, or WKB, or the variational principle. The RS perturbative technique is appropriate when the additional term in the Hamiltonian is small compared to the others. The other two are necessary when it isn’t. In this case, the perturbation term is small and so we can use that technique. So using the formula for the energy levels (RSDPT),



The first order correction is just:



where the |ψnℓm> are just the Hydrogenic atom wavefunctions. Well this would presume that 4 is already diagonal in the (n fixed) ψnℓm basis, i.e., that:



And it turns out to be so. I guess we can argue this is true by noting that |ψnℓm> (n fixed) forms a non-degenerate basis for the operators L2 and Lz. And p4 commutes with these. So |ψnℓm> form a diagonal basis of the p4 operator within the n = constant subspace. Going back to δEnℓm, we can make some algebraic manipulations to this expectation before trying to evaluate it. First,



Now the unperturbed states |ψnℓm> satisfy the equation:



and so we can write this expectation as:



where the unperturbed energy levels are of course:



To calculate these expectations, we can either do the integrals – not recommended – or we can do some more trickery. We will use the Feynman-Hellman equation:



So using the fact that these unperturbed wavefunctions we’re using satisfy the equation:



and using the Feynman-Hellman equation with λ = Z, we can say that:



where a0 is the Bohr radius,



So that’s one expectation. As for the other expectation, we’ll let λ = ℓ and repeat. We need to be careful about taking the derivative of E w/r to ℓ. As we increase ℓ, E must change, indirectly, because n must be changing with it to accommodate higher ℓ’s. Going back to our derivation of the energy levels, we’ll remember that n was shorthand for:



where N was the whole number specifying when the power series expansion of the radial function terminated. So really, we would should have:



Alright, now applying the FH equation:



Filling these expectations in, and using,



we have:



So we have:



These corrections lower the energy by a small amount, perhaps because a given relativistic kinetic energy corresponds to a lower ‘velocity’ than does a classical kinetic energy. But if the velocity is lowered, then the electron will sink further into the orbit, lowering its potential energy, and thus overall energy.

**Correction due to spin-orbit coupling**

Relativity is involved in another effect as well, namely that EM fields appear different in different inertial frames. For instance, consider a charge, q, moving with speed **v**. If we are moving alongside the charge, then we will measure the charge to be creating an electric field, **E**, given by:



On the other hand, if we are stationary, then the charge is moving, and will appear to be (and really is) creating an electric *and* magnetic field, given to first order in β = v/c by:



where **B** is given by the usual Biot-Savart law for a moving charge. So the moral of the story is that EM fields are perceived to be different in different inertial frames. This goes for dipole moments too. Consider being in the inertial frame of a spherical charge q, rotating about its own axis. In this frame it has a magnetic dipole moment, **μ**, but no electric dipole moment, **p**. If we step out of this frame, into one where the charge is moving with velocity **v**, then we will measure it to have not just a magnetic dipole moment of **μ**, but also an electric dipole moment, **p**, basically due to length contraction and stuff.

This goes for an electron orbiting a nucleus, and the additional relativistic interaction we’ve ignored so far is the interaction of the nuclear electric field with the electron’s relativistically acquired electric dipole moment, **p**. But rather than write down what this dipole moment **p** is from the nuclear rest frame, and calculate the interaction energy as Hint = -**p**·**E**, we just figure out the interaction energy from the electron’s inertial frame, cause it’s easier. Hopping aboard an inertial frame (also call this the ‘lab’ frame) instananeously at rest with respect to the electron (but not accelerating with the electron around the nucleus, so the frame just travels tangential to the electron’s orbit), we see two things. First, we see something unexpected (that we also would see in the nuclear rest frame – basically any inertial frame), and that is the electron’s reference frame appears to precess about its origin at the rate (recall the Poincare´ transformation file from Classical Mechanics and the discussion of Thomas precession):



How does this change the electron’s angular momentum and magnetic moment? Well the electron’s angular momentum with respect to its own precessing rest frame is **S**. And if we step outside this precessing rest frame into the aforementioned inertial frame, then we’d see that ωT changes the overall angular velocity of the electron, and therefore its angular momentum and effective magnetic moment, but its not clear how, since we can’t treat the electron as a classical object. So best we can say for now is:



Second thing we see is that the nucleus now appears to be orbiting around the electron with velocity -**v**, creating a magnetic field, **B**, in the process. And this magnetic field will interact with the electron’s effective magnetic dipole moment with energy HSO, given by:



But it’s uncertain how to find the μeff, so another option is to go back to:



But what is the ‘torque’ acting on our spin? Well it’s d**S**/dt. And in rest frame of the electron, d**S**/dt is just gγ**S×B** for sure. But in the lab frame, where we measure the HSO energy, d**S**/dt is not just **B**. Using a little bit of classical mechanics, you may recall that in fact,



where **ω** is the rate of precession of the rest frame. This formula has nothing to do with relativity and is just a geometric vector relation. So then we may write:



So we see that this adds a term to **B**, creating an effective **B**eff. = **B** – **ω**T/gγ. So then our real interaction energy is:



OK, let’s simplify the first term by filling in what **S** and **B** are, and then writing it in terms of the electron’s angular momentum for cosmetic purposes.



and the other term is:



which is negative half the other guy. Adding them together gives:



So this is the classical version of the interaction energy. To go to quantum mechanics we simply promote the observables to operators and so we have:



So our Hamiltonian, including the SO interaction would be:



Does **L**·**S** commute with itself? It must, but let’s check (implicit summation over indices).



Cool. More concretely, for instance,



Now let’s try to determine the eigenfunctions of H, perturbatively. We can use the same formula as before:



But once again, as per degenerate PT, we have to use the basis in the degenerate eigenspace of H0 that diagonalizes V1. This isn’t too hard actually. We’ll note:



and so we can write HSO as:



And we can see that, except for the 1/3 term, the eigenfunctions we’re looking for would be simultaneous eigenkets of L2, S2, and J2, i.e., |lsjmj>, or, more fully |nℓsjmj>. In truth, the 1/r3 term shouldn’t make much difference as an operator, and so we are going to replace it by its expectation w/r to these states (just going to quote the result):



so that now the |nℓsjmj> really do diagonalize our perturbation within the degenerate subspace. Then we’ll have:



So up to first order we have:



Doing some work on the eigenvalue correction…



So finally,



**Combined Correction**

Adding the two corrections together, gives (using the fact that s = ½ and j = ℓ ± 1/2):



Okay well let’s make s = ½, and specialize to j = ℓ + ½. Then we get:



Apparently we get the same final result if we make j = ℓ - ½. So we have:



which is the fine-structure correction to the energy levels. By the way, we get an interesting constant out of the ratio of an electron’s hydrogen atom ground state energy to its rest energy:



where we define the fine structure constant, α:

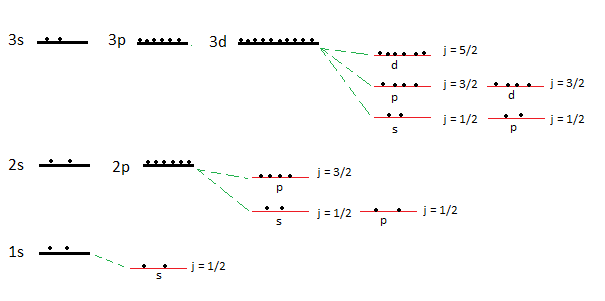


And in terms of this, we can write the energy correction as:



So evidently, the energy levels of the electrons in the H-atom do not depend solely on n, but also on j. Each electron can be characterized by the quantum numbers |nℓsjmj>. So now Enj will depend on the orbital, not just the shell. The correction will be negative, but less so as j increases. So the energy levels should more or less go up with ℓ. This trend congrues with the general model that if say the electron is orbiting the nucleus CCW with spin pointed up, then the nucleus is going CW w/r to the electron, and creating a B field pointing down, which is a positive energy situation, and which would be made more positive should the angular momentum of the electron increase.

Drew rough picture below, for a couple levels. In unperturbed model, energies are degenerate w/r to subshells. In perturbed model, the degeneracy splits according to j. Note some electrons in s and p subshells can have same j value (basically ℓ = 0, spin up = ℓ = 1, spin down, etc.), as can electrons in p and d shells for instance. That’s why we have duplicate j levels.



The use of all of this special relativity, and the emergence of j as the good quantum number, instead of ℓ and s separately hints at the fact that j is the ‘real momentum’ when incorporating special relativity, and that spin angular momentum is a relativistic effect. This bears out when we get to the Dirac equation, which fully incorporates relativity into quantum mechanics, well, except for particle creation/annihilation.